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RESEARCH ARTICLE OPEN ACCESS

Photoelectrochemical Conversion of Solar Energy into Electrical Energy

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Abstract
The photogalvanic cell comprising Toluidine Blue – Arabinose as dye – reductant couple were studied in presence of cationic surfactant Cetylpyridinium chloride (CPC). The maximum power output, the conversion efficiency and the storage capacity were noted 20.82 μW, 0.068% and 72 minutes respectively for developed cell.
The effect of pH, concentration of cell solution component (dye, reductant, surfactant), diffusion length, electrode area etc. on electrical output parameters of the cell were also examined under the investigation.
A tentative mechanism has been proposed.
Key words: Toluidine Blue, Arabinose, CPC, Photoelectrochemical Conversion, Storage capacity.

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I. Introduction

On photoelectrochemical effect [1,2], various effective works have been done using dye/reductant system especially with well known Thionine/Fe (II) [3-5]. The ethereal emulsion, leuco dye accumulating in the ethereal phase and gelatinizing agents were used to circumvent the problem of frequent backward reaction occurring between electrode active species in cell solution and studied the effect on cell's electrical output [6-8].

In the present work, we experimentally studied the Toluidine Blue – Arabinose system in presence of cationic surfactant CPC in photoelectorochemical cell.

II. Experimental

All the stock solutions of Toluidine Blue (1×10^{-3} M), Arabinose (1×10^{-2} M) and Cetylpyridinium Chloride (1×10^{-2} M) were prepared in double distilled water. 1N solution of NaOH was freshly prepared by standardization with1 N oxalic acid using phenolphthalein indicator in every experiment. Dye solution was stored in darkened container to protect light exposure. Prepared photogalvanic cell solution was taken into the blackened H shaped container. A platinum foil electrode (1 cm^2 electrode area) was immersed into one limb of container which contains a transparent window through which electrode was exposed to light and a saturated calomel electrode (SCE) was immersed in another one. A water filter was used between the cell and light source (200 W tungsten lamp) to prevent the reactive system from thermal radiation.

A digital pH meter (Systronics model 335) and a microammeter (MO-65) were used to measure photopotential, photocurrent respectively produced by the developed photogalvanic cell. A load resistance was used to apply desired load in microammeter circuit to establish current and power output characteristics of the cell.

The experimental set-up is shown in Fig. 1.

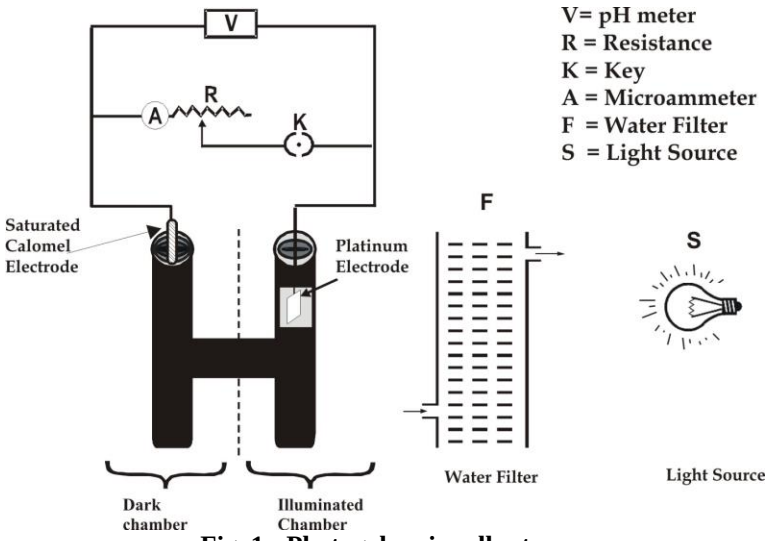

Fig. 1 : Photogalvanic cell set-up

III. Results and Discussion

Effect of pH

Experimental observation (Table I) shows that photogalvanic system Toluidine Blue – Arabinose – CPC is sensitive towards the pH of the cell solution. The photopotential and photocurrent increases with the increase in pH, reaches maximum at pH = 12.71 and then decreases with further increase in pH.

At pH = 12.71, developed photogalvanic cell produced maximum power output, it may be due to better availability of the reductant's donor form at this particular pH.

Effect of variation of CPC concentration

It was examined that electrical output of the cell initially increases and then decreased with the increase in concentration of CPC. At [CPC] = 5.6 x 10^{-4} M, cell produced maximum power output and further increases in the concentration of surfactant resulted into a fall in output (Fig. 2).

The Toluidine Blue – Arabinose system was studied in absence of CPC and we found decreased value of electrical output. It indicates that there may be presence of the charge transfer interaction between the dye-surfactant and it should be effective in enhancement of cell performance.

The photoejection of electrons from dye-surfactant system in terms of tunneling of photoelectrons from miceller to aqueous phase was observed by Alkaitis et al. [9].

Yoshikiyo Moroi et al. studied the photo-induced reduction of cupric ions by organic donors in functional surfactant assemblies, storing a large fraction of the light energy originally converted into chemical energy during the photoredox process [10].

Effect of variation of dye (Toluidine Blue) concentration

The photogalvanic system with variation of dye concentration was experimentally studied (Fig. 3). It was observed that system with [dye] = 2.8 x 10^{-5} M worked with optimum power output. The cell's electrical output was found decreased when dye concentration changed from above mentioned value.

H. Gerischer [11] and R. Memming [12] reported experimental results of the work on dye sensitization of electrodes in photoelectrochemical cells that only the dye molecules (or ions) directly absorbed on the surface of the electrode causes the photocurrent, not those in the bulk of the solution. So, in presence of higher concentration of the dye, major portion of light is absorbed by the dye molecules present in the path/bulk of the solution, hence the dye molecules in the vicinity of platinum electrode will not obtain the desired light intensity. In presence of lower concentration of the dye, there should be low availability of dye molecules to excite and to donate electron to the platinum electrode.

Effect of variation of reductant (Arabinose) concentration

Variation of Arabinose concentration effects the photopotential and photocurrent (Fig. 4) in the similar manner as that of the dye concentration variation due to photogalvanic behaviour of the system which is result of dye-reductant interaction under the light condition.

The higher reductant concentration shows decreases in electrical output because the large number of reductant molecules may hamper the way of dye molecules towards the platinum electrode in the desired time. The lower concentration of reductant also decreases the electrical output as lesser number of reductant molecules will be available for electron donation to reduce the dye molecules.

Effect of electrode area and diffusion length

The effect of electrode area on the photocurrent generation was also studied and represented graphically in Fig.5. Maximum photocurrent (i_{max}) regularly increased but equilibrium photocurrent (i_{eq}) negligibly decreased with increasing electrode area.

The platinum foil electrode and saturated calomel electrode were immersed in two limb of cell solution container of H shaped. The distance between these two electrodes is called diffusion length. Effect of the diffusion length on the current parameters of the cell (i_{max}, i_{eq} and initial rate of generation of photocurrent) was observed by using different dimensions H-shaped containers (Table II). i_{max} and rate of initial generation of current increases with diffusion length while i_{eq} shows a negligibly small decreasing behaviour.

The effect of variation of diffusion length on photocurrent generated by photogalvanic cell can be understood by the electrode active species occurred in cell solution. The probable electrode active species are given in Table III.

Table III.
Probable electrode active species

In illuminated compartment	In dark compartment
Dye	Oxidized form of reductant
Semi or Leuco form of dye	Oxidized form of reductant
Semi or Leuco form of dye	Dye

If oxidized reductant acts as electrode active species in dark compartment, it will diffuse from illuminated compartment to the dark compartment to get electron from SCE. If this position occurs, photocurrent must decreas with increase in the diffusion length. But it was not observed in our experiment. Therefore, we reached at the conclusion that reduced dye Toluidine Blue and dye Toluidine Blue acts as electrode active species in illuminated and dark compartment, respectively in support of experimental observation. However, reductant and oxidized reductant can act as the electron carrier.

Current and power output characteristics, conversion efficiency and storage capacity of the cell

The cell's current – voltage (i-V) characteristics (Fig. 6) is shown between the current and potential values, measured between the V_{oc} (open circuit voltage) and i_{sc} (short circuit current) by applying external load in microammeter circuit. Power output characteristics of the cell is shown in Fig. 7.

By i-V curve we obtained a point where product of current and potential found maximum called power point. Storage capacity of the cell denoted by $t_{1/2}$ is the measure of performance of the cell, observed 72 minutes by keeping the cell at power point stage in dark and noted the time required in fall of power output to its half value (Fig. 8).

The conversion efficiency and fill factor of the cell (with platinum foil electrode of 1 cm^2 electrode area) was determined 0.0689% and 0.285 respectively by following formula :

$$\text{Conversion efficiency} = \frac{V_{pp} \times i_{pp}}{10.4\ mW/cm^2} \times 100\% \quad \ldots(1)$$

$$\text{Fill Factor} = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \quad \ldots(2)$$

where V_{pp} and i_{pp} represents the value of potential and current at power point, respectively.

Mechanism

G. Oster et al. worked on photochemistry of dyes in solution and demonstrated that chemically reactive species is the triplet state of the dye. Specially, when certain dyes are excited by light in the presence of electron donating substances, the dyes are rapidly changed into colourless (reduced) form. The dye is now a powerful reducing agent and will donate electrons to other substances, with the dye being returned to its oxidized state [13].

On the basis of above studies, a tentative mechanism has been proposed as follows :

Illuminated Compartment

$$\text{Dye} \xrightarrow{h\nu} \text{Dye}^{*} \longrightarrow \text{Dye}' \qquad \ldots(1)$$

(Ground state) (First excited state) (Triplet state)

$$\text{Dye}' + R \longrightarrow \text{Dye}^{-} + R^{+} \qquad \ldots(2)$$

(semi or leuco form of dye)

At platinum electrode :

$$\text{Dye}^{-} \longrightarrow \text{Dye} + e^{-} \qquad \ldots(3)$$

Dark Compartment

At SCE:

$$\text{Dye} + e^{-} \longrightarrow \text{Dye}^{-} \text{ (semi or leuco form of dye)} \qquad \ldots(4)$$

$$\text{Dye}^{-} + R^{+} \longrightarrow \text{Dye} + R \qquad \ldots(5)$$

where Dye, Dye^{-}, R and R^{+} represents the Toluidine Blue, reduced form of dye, reductant and oxidized form of reductant, respectively.

IV. Conclusion

The phoelectrochemical system Toluidine Blue – Arabinose – CPC was examined for solar energy conversion and storage. Conversion efficiency of the developed cell was found lower but storage capacity was obtained enthusiastic.

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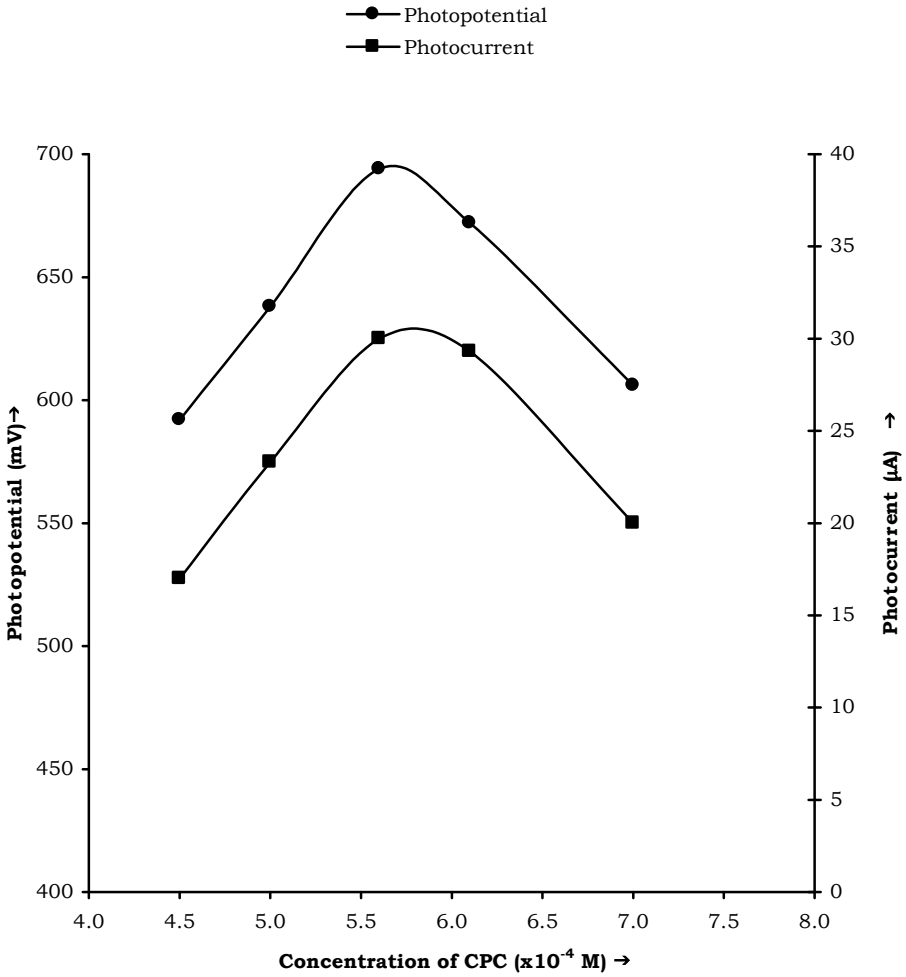

Fig. 2. VARIATION OF PHOTOPOTENTIAL AND PHOTOCURRENT WITH CPC CONCENTRATION

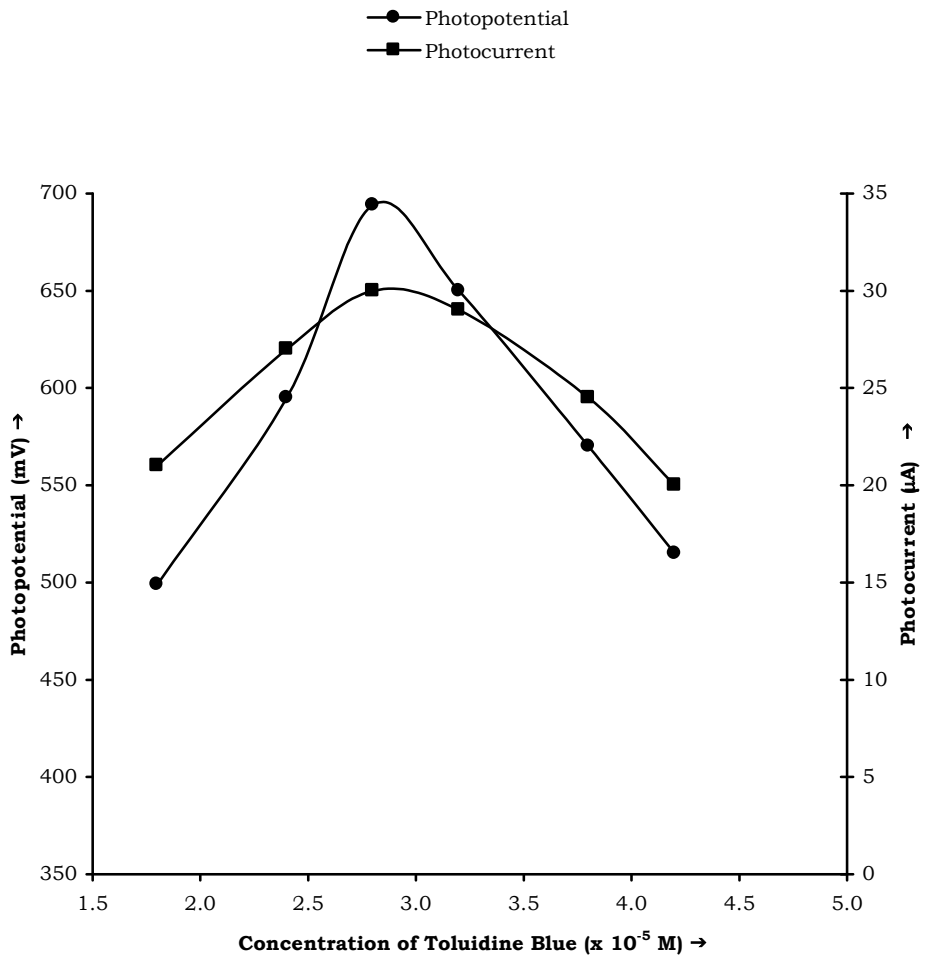

Fig. 3. VARIATION OF PHOTOPOTENTIAL AND PHOTOCURRENT WITH TOLUIDINE BLUE CONCENTRATION

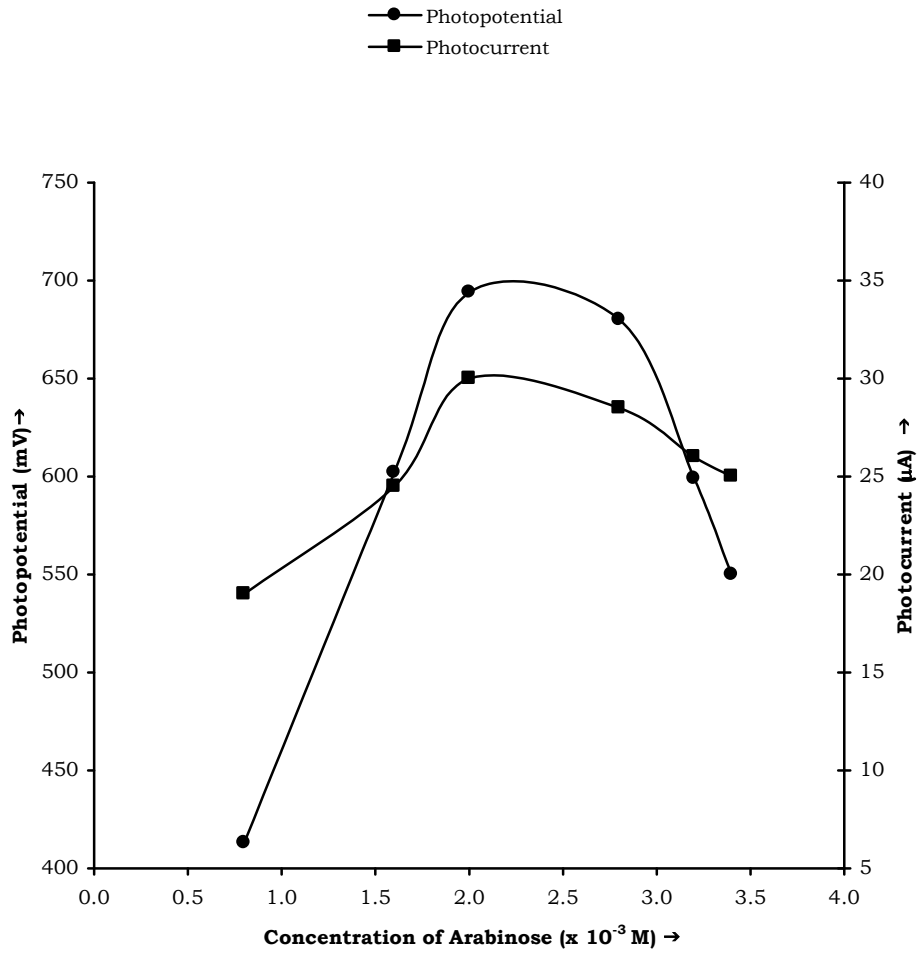

Fig. 4. VARIATION OF PHOTOPOTENTIAL AND PHOTOCURRENT WITH ARABINOSE CONCENTRATION

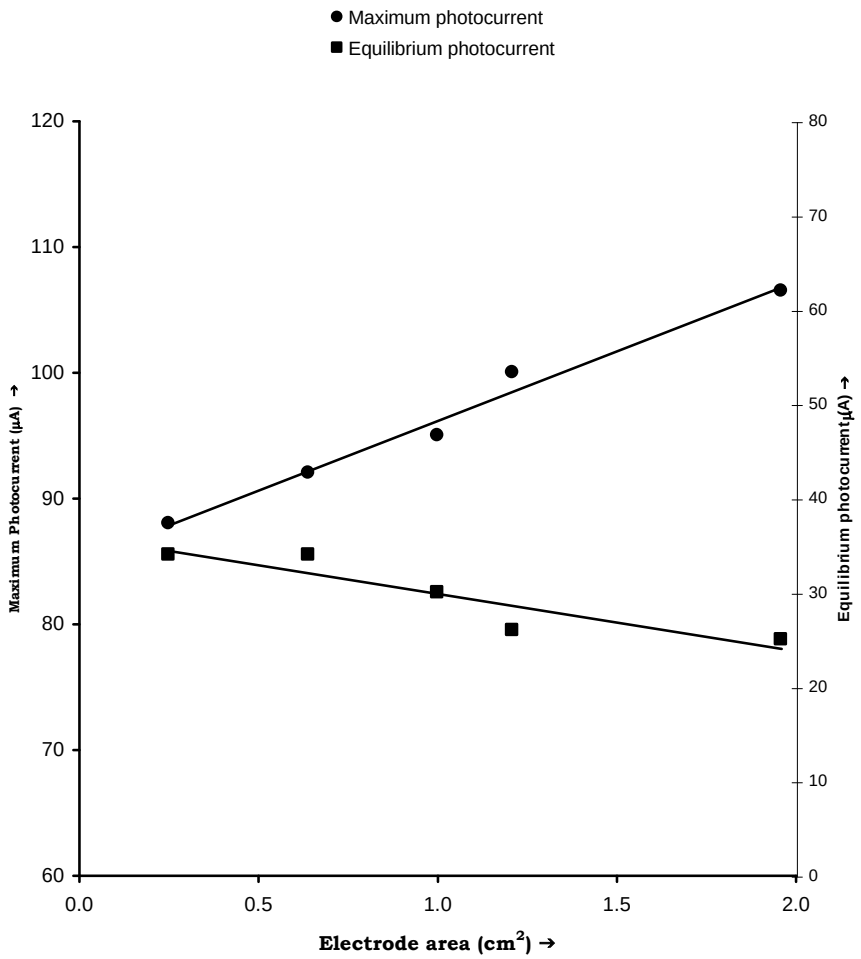

Fig. 5. VARIATION OF CURRENT PARAMETERS WITH ELECTRODE AREA

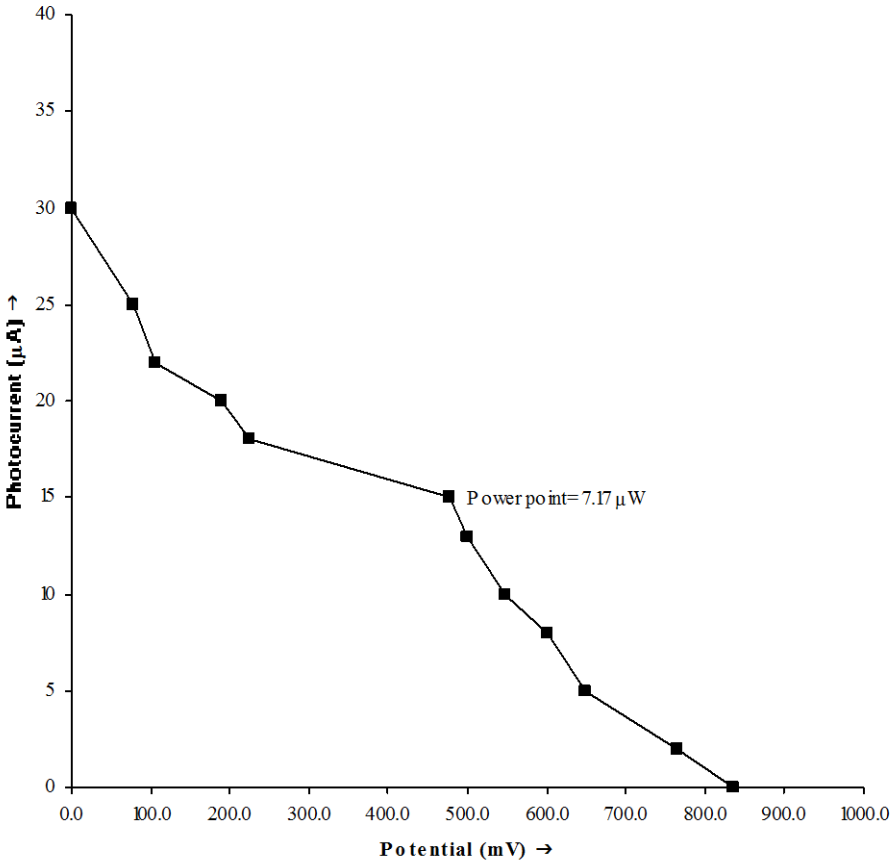

Fig. 6. CURRENT-VOLTAGE (i-V) CURVE OF THE CELL

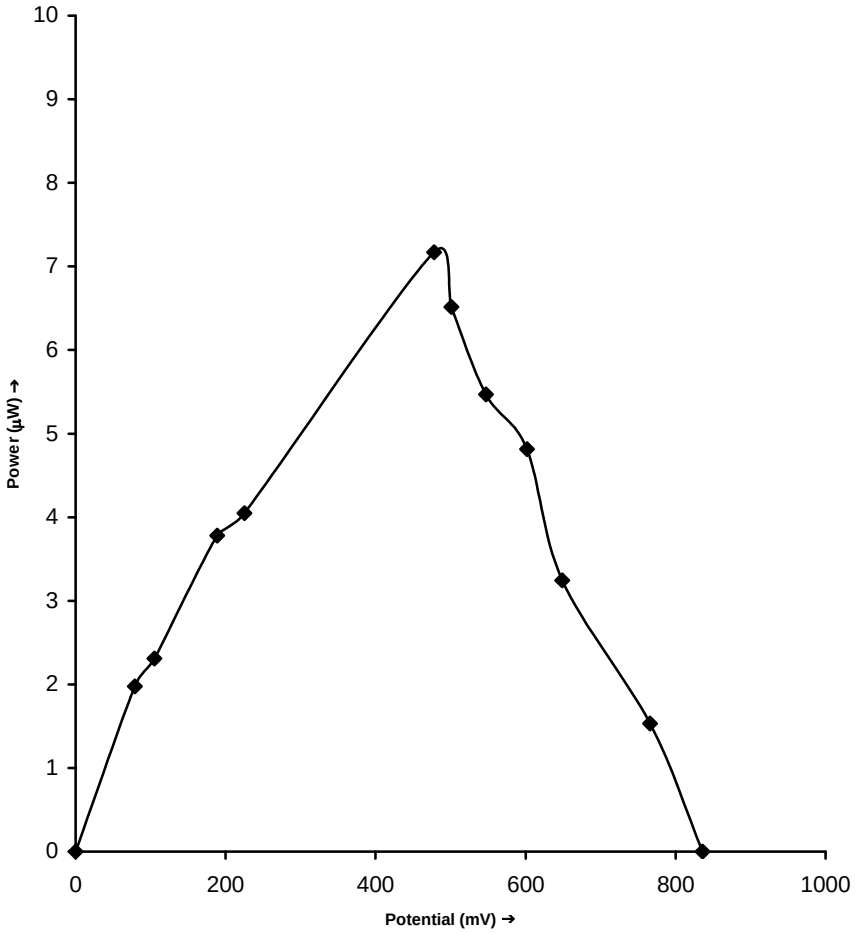

Fig. 7. Power-Voltage Curve

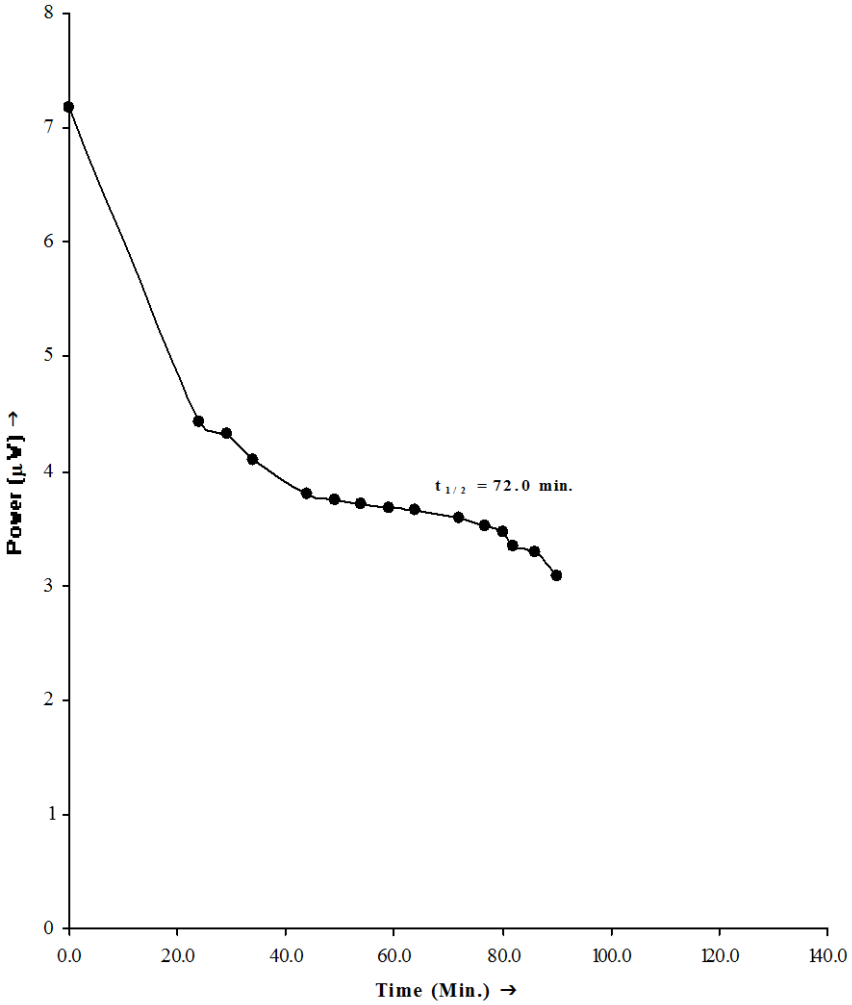

Fig. 8. PERFORMANCE OF THE CELL

Table I
Effect of variation of pH

pH	Photopotential (mV)	Photocurrent (μA)	Power (μW)
12.50	580.0	24.0	13.92
12.60	620.0	28.0	17.36
12.71	694.0	30.0	20.82
12.85	624.0	26.5	16.53
13.00	585.0	25.0	14.62

[Toluidine Blue] = 2.8 x 10^{-5} M; [Arabinose]=2 x 10^{-3} M; [CPC]= 5.6 x 10^{-4}; Light Intensity = 10.4 mWcm^{-2} ; Temperature = 303 K

Table II
Effect of Variation of Diffusion Length

Diffusion Length D_L (mm)	Maximum Photocurrent i_{max} (μA)	Equilibrium Photocurrent i_{eq} (μA)	Rate of initial Generation of Current (μA min^{-1})
35	88	33.0	5.86
40	92	31.5	8.13
45	95	30.0	6.33
50	96	28.5	6.40
55	102	28.0	6.80

[Toluidine Blue] = 2.8 x 10^{-5} M; [Arabinose]= 2 x 10^{-3} M; [CPC] = 5.6 x 10^{-4}; pH = 12.71; Light Intensity = 10.4 $mWcm^{-2}$; Temperature = 303 K